

**BEAMLINE**  
X27C

**PUBLICATION**

Zhu, L. et al. "Nanotailored crystalline morphologies in hexagonal perforated layers of a self-assembled PS-*b*-PEO diblock copolymer," *Macromolecules*, **35**, 3553 (2002).

**FUNDING**

National Science Foundation (DMR)  
Department of Energy (DOE)

**FOR MORE INFORMATION**

Lei Zhu, Prof. University of Akron, Ohio  
lei@polymer.uakron.edu

## Tailor-Made Polymer Nanocrystals

Lei Zhu<sup>1</sup>, Ping Huang<sup>1</sup>, William Y. Chen<sup>1</sup>, Qing Ge<sup>1</sup>, Roderic P. Quirk<sup>1</sup>, Stephen Z. D. Cheng<sup>1</sup>, Edwin L. Thomas<sup>2</sup>, Bernard Lotz<sup>3</sup>, Benjamin S. Hsiao<sup>4</sup>, Fengji Yeh<sup>4</sup> and Lizhi Liu<sup>4</sup>

<sup>1</sup>University of Akron; <sup>2</sup>Massachusetts Institute of Technology; <sup>3</sup>Charles Sadron Institute, Strasbourg, France; and <sup>4</sup>State University of New York at Stony Brook

*Chemicals made of chain molecules called block copolymers can self-assemble into various ordered structures, such as lamellae, cylinders, and spheres. Using self-assembled crystalline-amorphous block copolymers, scientists have grown ordered polymer nanocrystals, which are expected to be used in advanced optical applications. X-ray scattering studies at the NSLS revealed that, simply by varying the crystallization temperature, the tiny crystals can orient in different directions with respect to the interface between the crystalline and amorphous domains in the copolymer. Crystal growth can also be tailored in specific directions by conforming to the geometry of the block copolymer nanophases at high temperature.*

Polymers in a confined space of a few nanometers, or billionths of a meter, are expected to exhibit a different structure, stability and morphology than ordinary bulk polymers. For instance, the polymers can be confined in mesoporous inorganic materials, which are made of pores that are 2 to 50 nanometers in diameter. But if no specific interactions occur between the inorganic material interfaces and the crystalline polymers, it is very difficult to drive polymers into the nanopores.

To avoid this constraint, a team of scientists from the University of Akron in Ohio, the Massachusetts Institute of Technology, the Charles Sadron Institute in Strasbourg, France, and the State University of New York in Stony Brook has been successfully using mesophases (typically ordered phases with sub-micron sizes) of a crystalline-amorphous diblock copolymer – which form by simultaneous self-assembly process – to study confined polymer crystallization in nanospaces.

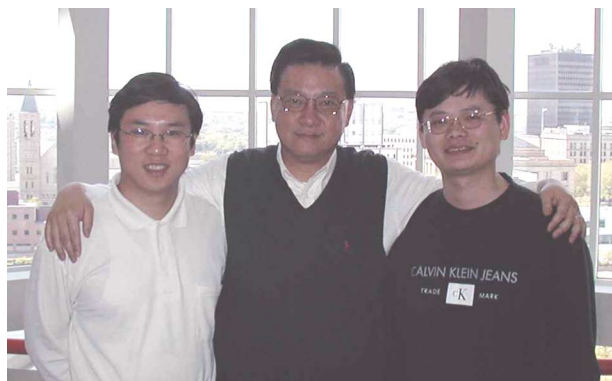
ene oxide (PS-*b*-PEO), is made of polystyrene (PS), an amorphous polymer with a glass transition temperature of 100 degrees Celsius, and polyethylene oxide (PEO), a crystalline polymer with an equilibrium melting temperature of 69 degrees Celsius. Because of their distinct chemical nature, PS and PEO strongly segregate from each other, so after the PS matrix glassifies, the crystallized PEO blocks are completely confined within the nanospaces of the copolymer.

The PEO nanocrystals were investigated on macroscopically-oriented (a single domain in microns or even millimeters) PS-*b*-PEO

single crystals using simultaneous small and wide-angle X-ray scattering (SAXS and WAXS) techniques at the NSLS's Advanced Polymer beam line X27C. The detailed experimental setup is displayed in Figure 1.

High-resolution SAXS revealed that the PS-*b*-PEO sample with 0.39 percent of PEO in volume exhibits a hexagonally perforated layer (HPL) phase, where the PS and PEO layers are alternating and each PEO layer is made of two-dimensionally packed PS perforations, as shown in Figure 2.

The researchers also studied how the nanolayers and nano-PS cylinders in the PEO layers affect the crystallization behavior of the PEO blocks. The WAXS results showed that the PEO crystal orientation in the HPL phase changes with the crystallization temperature. At low temperatures, the PEO crystals preferentially arrange parallel to the layer plane (Figure 2a top), while above zero degree Celsius, the crystals become inclined with respect to the layer plane (Figure 2b top). The team also no-



Authors (from left): Lei Zhu, Stephen Z. D. Cheng and Ping Huang.

The copolymer, called polystyrene-*b*-polyethyl-

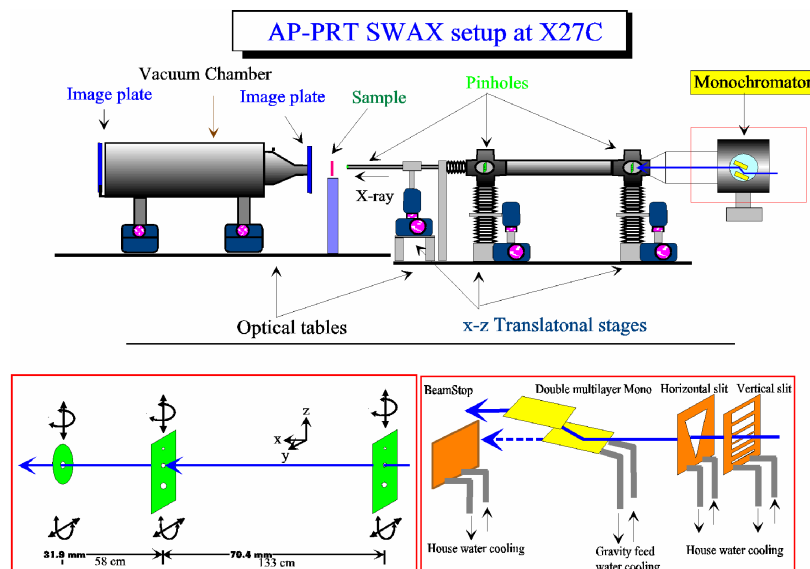
ticed that the ribbon-like PEO crystal grows along the arrays of the hexagonal PS perforations (Figure 2b bottom).

Surprisingly, the WAXS experiments showed that crystal orientation forms in an early stage of crystallization with a crystallinity of

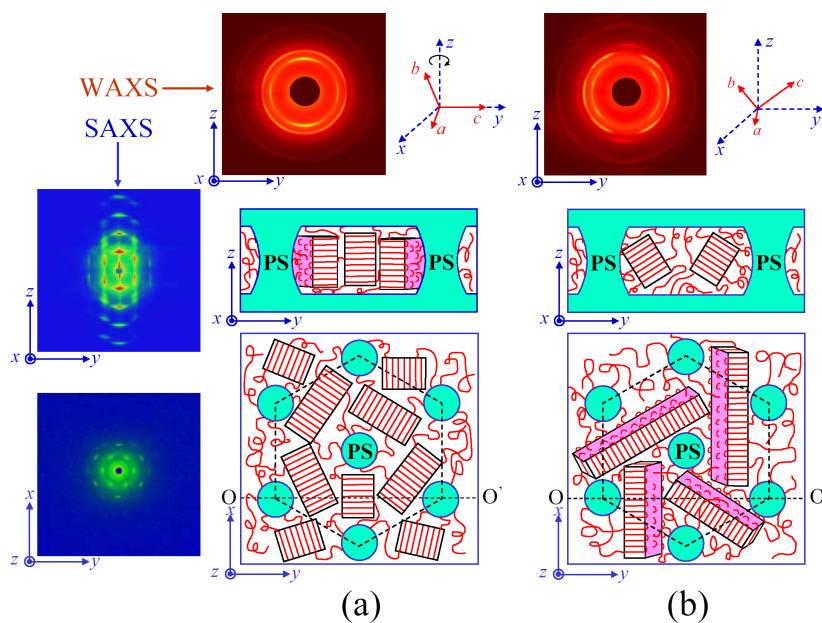
$\sim 7$  weight percent. The early stage crystal orientation clearly reflects the confined effect on polymer crystallization in nanospaces.

These results not only show the scientists' ability to manipulate polymer crystalline morphologies confined in nanospaces, but also

reveal the details of polymer crystallization on the nanoscale. Further study will investigate the crystal orientation mechanism and explore polymer crystallization in compounds with more elaborate mesophases, such as double gyroids.



**Figure 1.** Experimental setup for simultaneous SAXS and WAXS at beamline X27C at NSLS.



**Figure 2.** Nano-tailored PEO crystalline morphologies at (a)  $-50\text{ }^{\circ}\text{C} \leq T_c \leq -10\text{ }^{\circ}\text{C}$  and (b)  $T_c \geq 0\text{ }^{\circ}\text{C}$ . A nanophase is defined by  $x$ ,  $y$ , and  $z$ , and crystal unit cell axes are  $a$ ,  $b$ , and  $c$ . The top view of the HPL phase is shown at the bottom, and the side view at the top.